

## Distribution of mercury in the aquatic environment at Almadén, Spain

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Received 4 December 2001; accepted 5 July 2002

**“Capsule”:** Concentrations of mercury in water, sediment and bivalves near the world’s largest mercury mine is documented.

### Abstract

The world’s largest mercury mine is placed at Almadén, Spain. However, there is a lack of information about the environmental impact of these mining activities in the ecosystem that surrounds this area. The aim of this article is to document the concentration of mercury in waters, sediments and bivalves of the aquatic system impacted by historic mine wastes. Simultaneously, a comprehensive study has been undertaken to characterise this hydrosystem and to determine the influence of some major physico-chemical parameters on the fate of mercury. Samplings were carried out for the last few years. Concentration of mercury in waters ranged from not detectable to 20 µg/l. For the sediments study, samples have been taken both from contaminated and non-contaminated sites within the basin. The regional background mercury concentration is higher than values typically cited for natural backgrounds. At exposed sites the mercury concentrations between 5 and 1000 µg/g were measured. These values are one to four order of magnitude greater than regional background levels. In the comparison between the results obtained at the present moment and those available for the 1974–1977 period, a general diminution of mercury levels is observed. Mercury concentrations in fresh water bivalves ranged between 1 and 4 µg/g (d.w.), with around 30% as monomethylmercury. In the discussion of the implications for risk assessment data available for other areas affected both for mine activities and mercuriferous belt are included.

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**Keywords:** Mercury; Almadén; Spain; Water; Sediment; Bivalves; Mine activity

### 1. Introduction

The Almadén area is unusual for a number of reasons, including its location in a natural mercuriferous belt (before the mining began the area contained about a third of the earth’s total known mercury resources), high and sustained levels of anthropogenic mercury inputs (50% of the free world Hg production in 1972) and long exposure time (~2000 years). Effluents are dispersed to both terrestrial and aquatic ecosystem of the region, which is exposed to elevated levels of environmental mercury derived from out-gassing, rock weathering and from the mine/smelter processes.

However, neither the extension nor the effect of this dispersion is known. Only a few studies have been conducted to evaluate the environmental impact and

potential hazards related to mercury contamination in the ecosystem that surrounds this area. To our knowledge, the most extensive study of mercury distribution was that carried out by ORNL (Oak Ridge National Laboratory, USA) in the 1974–1977 years. The results were published as an internal report in 1980 (Hildebrand et al., 1980). In 1979 Lindberg et al. reported the results of a study on mercury uptake in plant growth on surface soils collected near the Almadén mine; the rate of volatilisation of mercury from these soils was also determined in a laboratory experiment. In addition, the distribution of mercury in the vegetation at Almadén area, evaluated during the ORNL field campaign, was published by Huckabee et al. in 1983. Recently, atmospheric mercury levels around the Almadén refining complex were determined in two field campaigns carried out in 1993–1994 (Ferrara et al., 1998). High mercury concentrations (0.1–5 µg/m<sup>3</sup>) were measured over the village of Almadén in the prevailing wind direction

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(west and southwest). The total mercury flux into the atmosphere was estimated to range from 600 to 1200 g/h. Even at considerable distance from the main emission sources (5–10 Km) in a easterly direction, high air mercury levels (0.05–0.1  $\mu\text{g}/\text{m}^3$ ) were observed.

A significant portion of Hg-contaminated waste tailing generated by the mine activity has directly or indirectly entered the aquatic environment, mainly the Valdezogues River that runs east–west along the Almadén area. The study of the aquatic system is of great interest due to the possibility of mercury transformation and accumulation in this environment. However, the available data are very ancient (more than 20 years) and significant events have happened since then affecting both spatial distribution and mercury emissions. Thus, when the ORNL's work was performed the only mine in activity was that placed in Almadén city, but after two new mines started to work in the area, “El Entredicho” (1979) and “Las Cuevas” mines (1988). In any case, the Almadén refining complex continued to be an important source of mercury because all the roasting processes were carried out at this place. A treatment plant for mine wasting started to work in 1977. And, lastly, the mercury emissions have been drastically reduced. In 1990 the price collapsed and caused a crisis, with no production in 1991–1992 and very low output (20,000 flasks of mercury; 690 t) in 1993–1994 in comparison with the peak production reached in 1941 (82,000 flasks).

The present work reports the results obtained in an integrated program carried out to assess the distribution of total and mono-methylated mercury (MMHg) in the aquatic environment of the Almadén area (Rodríguez, 1999). Simultaneously, a comprehensive study has been undertaken to achieve a characterisation of this hydro-system. No previous data are available and this information could be useful to understand the fate of mercury within the system. Total mercury contents in waters and sediments are reported. The chemical speciation, fractionation and availability of mercury in sediments have been previously published (Rodríguez et al., 2000).

The final feature of this issue has been the mercury evaluation in the biota of the Valdezogues River. Mercury in the environment can be converted from inorganic forms to the more toxic and bio-magnification prone monomethylmercury (Craig, 1986; Choi and Bartha, 1994; Grieb et al., 1990). MMHg concentration increase in aquatic organisms that are higher in the food chain and the main pathway for mercury exposure in humans is fish consumption (May et al., 1987). Therefore, the study of exchange of mercury among the abiotic and biotic environment compartments is of great interest. Taking into account the literature (Goldberg, 1975; Claisse, 1989; Cossa, 1988), it was considered that a fresh water bivalve (*Unio pictorum*) that lives in the Valdezogues River could be useful as a monitoring

target organism at the Almadén area. Several reasons support this fact. Firstly, they are organisms dwelling on or in the sediment so it could potentially be important for the transfer of mercury from the contaminated sediments. Secondly, they are very similar to marine mussels that have been used as biological indicators of pollution for many years. Also, they have been used to carry out studies of the bioavailability of sediment-bound methyl and inorganic mercury (Gagnon and Fisher, 1997). Anyway, no systematic study of this aspect was carried out, thus results reported here should be regarded only as a first approach.

Special attention has been paid to the evaluation of mercury pollution state at Almadén area because the baseline for addressing human health and ecological risk is likely to be higher in sites situated within the mercuriferous belt. Thus, the mercury state of pollution at Almadén area has been determined not only with respect to general background levels proposed in the bibliography but also by comparison with regional background and with values found in other areas affected both by mine activities and mercuriferous belt: Carson River System (Gustin et al., 1994; Bonzongo et al., 1996a; Wayne et al., 1996; Bonzongo et al., 1996b) and Kuskokwim Mountains Region (Gray et al., 1994; Gray et al., 1996) in North America; and Idrija (Gosar et al., 1996; Horvat et al., 1999; Hines et al., 2000; Hess, 1991) and Monte Amiata (Barghigiani and Ristori, 1994; Ferrara et al., 1991) in the Mediterranean area.

## 2. Methods

### 2.1. Study area

The Valdezogues River runs east–west along Almadén area, which lies on a temperate, semiarid environment with an average annual rainfall of 500 mm. Flows in the river ranged from little to none during late summer, while in winter and spring flooding events occur. The area under investigation is a section of the Valdezogues River drainage basin (Fig. 1), which extends from the upper river downstream to the recently built La Serena dam (3231  $\text{Hm}^3$ ), the present terminus of the river.

Nine stations were chosen based on their location relative to known Hg-contaminated sites. The introduction of Hg from contaminated mine tailings occurs primarily at El Entredicho mercury mine, where a dam was constructed to divert the Valdezogues River. Two sampling stations were located there, station 1 in El Entredicho dam (5.37  $\text{Hm}^3$ ) and station 2 after El Entredicho mine. The remaining sampling stations were located downstream from this site, station 6 was placed in a dam (Castilseras dam, 5.30  $\text{Hm}^3$ ) constructed for irrigation uses, and station 8 is the only one located after the Almadén mercury mine tailings. The station 9

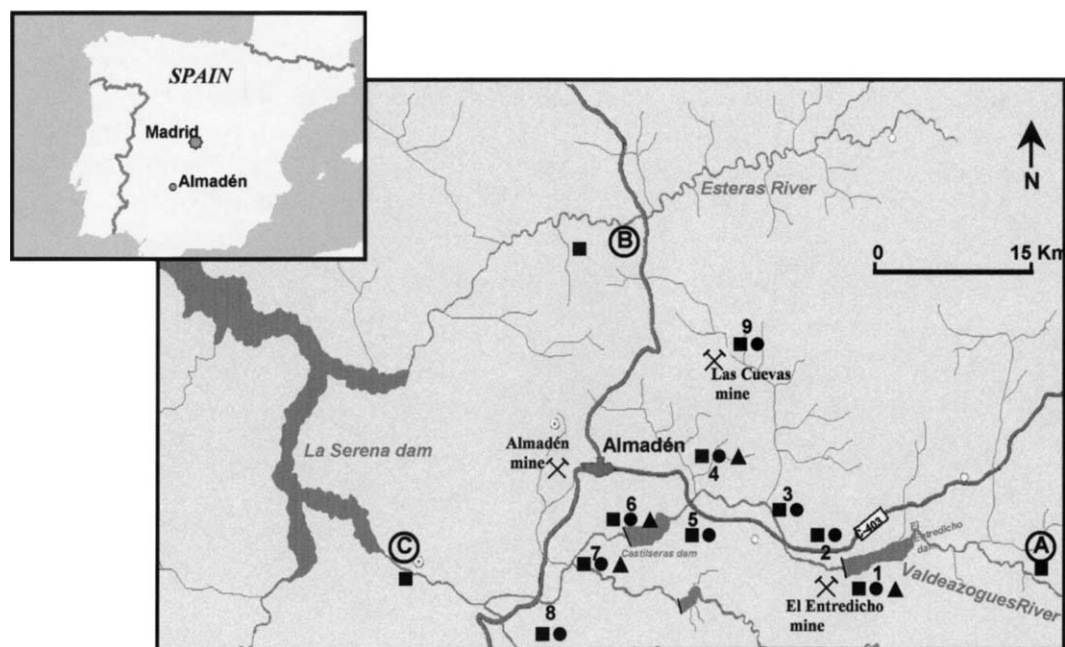


Fig. 1. Map of Almadén area showing the sampling stations for waters (&z.cirf;), sediments (■) and bivalves (▲). Solid circles with different letters indicate the background sediment samples (●).

was located in a stream that runs close to Las Cuevas mine. This stream enters the Valdezogues River after running 10 km.

To determine the baseline or background mercury levels in sediments from this area, two additional stations were established outside the direct mine tailings but within the mercury belt. The station A was located 5 km upstream the El Entredicho mine and a control station was selected on the Esteras River (Station B) because no mercury sources are known there. With the aim of evaluating the extent of mercury dispersion, the station C was established on the Valdezogues River just before the confluence to La Serena dam (Fig. 1).

## 2.2. Sampling and chemical analysis of surface waters

Water samples were collected in nine sampling seasons (from autumn 1995 to autumn 1997) from the nine sampling stations selected in the Valdezogues River (Fig. 1). Water samples were collected about 50 cm under the surface on 1-l Pyrex glass with neck and PP-screw-capwal bottles. Twenty-four parameters have been evaluated in each sample. The determination of pH, water temperature, nitrite and ammonium were performed in situ. Ionic chromatography, spectrophotometry and oxidability analyses were performed within 24 h after sampling. All glassware used was cleaned with detergent, thoroughly rinsed with tap water, soaked in a 10%  $\text{HNO}_3$  solution overnight and finally rinsed with Milli-Q water. For sample collection, bottles were rinsed three times with the river water before being filled. The water samples for analysis of metals were immediately

acidified (1% nitric acid). After sampling collection, and during transportation to the laboratory, samples were stored on ice. All the samples were filtered through a pre-acid cleaned glass filter. Analytical parameters have been determined with reference to official methods currently suggested (APHA, 1992; Rodier, 1981). Metals were analysed using atomic absorption, both flame (Varian, Model Spectraa 300) and electrothermal atomization (Varian, Model Zeeman 400). To determine total mercury in water an oxidation procedure ( $\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{KMnO}_4 + \text{K}_2\text{S}_2\text{O}_8$ ) was used, the excess of oxidant was eliminated by hydroxylamine sulfate addition (APHA, 1992). The mercuric ions were reduced to  $\text{Hg}^0$  using  $\text{SnCl}_2$  and subsequently the determination was carried out by cold-vapour atomic absorption spectrometry (CV-AAS) using a Varian vapour generation accessory Model VGA-76. Mercury detection limit was  $0.10 \mu\text{g/l}$ . Milli-Q water blanks were subjected to the same operations (storage, filtration, analysis) as real samples to control pollution during sample manipulation.

## 2.3. Sampling and chemical analysis of sediments

In autumn 1997 12 sediment samples were collected from the Valdezogues River basin and background selected sites (Fig. 1). Composite samples were scooped from the surface 5 cm of the sediment and returned to the laboratory in polyethylene bags. The samples were air-dried and sieved to separate the  $<2\text{-mm}$  size fraction. The samples were ground with an agate mortar to a particulate size of  $63 \mu\text{m}$ , which was retained for analysis.

The sediment samples, taken at the same nine points that waters, were characterised by determination of 25 physico-chemical parameters using standard methods (Jackson, 1982; Chapman, 1991; Kim, 1996). For total metals analysis, different from mercury, samples were digested with *aqua regia* and hydrofluoric acid in a closed system (Parr bombs) using microwave-heating. Approximately 50 mg of dried sediment were weighed into a PTFE bomb and then 0.5 ml of *aqua regia* plus 3.0 ml of hydrofluoric acid were added. The vessel was put into the microwave transparent body of the Parr 4782 bomb and closed tightly by hand. The system was placed in the microwave oven on the rotating Plexiglass tray and irradiated for 90 s at full power (800 W). The bomb was cooled and unscrewed. Immediately 10 ml of water and 2.8 g of  $\text{H}_3\text{BO}_3$  were added. Since no residue was obtained, the solution was directly transferred into a 100-ml polyethylene volumetric flask without filtration, made up to volume and stored in plastic vials at 4 °C for further analysis (Berzas et al., 1999).

For mercury analysis an extraction procedure with concentrated nitric acid in the same closed microwave system was developed. Briefly, 0.5 g of river sediment was weighted into the microwave transparent body of the Parr 4782 bomb and 2.5 ml of nitric acid (conc.) were added. The system was closed tightly by hand and it was placed in a domestic microwave oven and irradiated for 70 s at full power (800 W). The bomb was then cooled and the sample was filtered through an Albet type 1238 filter paper into a calibrated flask and made up to volume (10.0 or 25.0 ml) with Milli-Q water. The determinations were carried out by atomic absorption using CV-AAS after  $\text{SnCl}_2$  reduction for mercury analysis. The detection limit was 30.0 ng/g (Berzas et al., 1998a,b).

To test the accuracy of the methods for mercury total and other metal determinations three reference materials were analysed, they were GBW08301 (river sediment), GBW07311 (stream sediment), GBW07310 (stream sediment) from the National Research Centre for CRM of China. The application of a *t*-test for comparison showed that the certified and calculated values do not differ significantly at a level of significance of 95%.

#### 2.4. Sampling and mercury analysis of bivalves

Bivalve samples were obtained by hand picking at four locations (Fig. 1), from spring 1996. However, the population was found to be very restricted and difficult to access (only 30 individuals were collected). Owing to the limited number of available individuals, there are neither samples from all the sampling stations nor from all the seasons.

After sampling, the bivalves were put into plastic bags and transferred to the laboratory where they were stored at (–18 °C) until dissection. Soft tissues were removed from the shells. A pooled sample was prepared

with all the bivalves collected from a station at a period, this corresponds between three and six individuals. Tissues were ground, lyophilised for 8 h and ground again. Then, the ground tissues were lyophilised overnight. Finally, the samples were homogenised to a powder and kept in polyethylene bags at –18 °C until analysis.

For total mercury analysis, samples were digested by nitric acid treatment in a closed microwave system. Approximately 0.2 g of dry mass was weighted in a Parr 4782 bomb and 2.5 ml of nitric acid was added. The closed vessel was microwave extracted (800 W, 90 s). Since a clear solution was obtained, the sample was directly made up to a known volume (10.0 mL). The detection limit was 11.4 ng/g. (Berzas et al., 1998a,b). The determination was carried out by atomic absorption using CV-AAS after  $\text{SnCl}_2$  reduction. The accuracy of the methodology was tested by analysing the TORT-1 lobster hepatopancreas (National Research Council of Canada) and the GBW 08571 mussel tissue (National Research Center for CRM, China) reference material. The total mercury concentrations found were within the certified values.

Mercury species were quantitatively extracted from samples with tetramethylammonium hydroxide (TMAH) using an open microwave system as previously described in the literature (Tseng et al., 1997). The determination of mercury species was performed by an automated on-line hydride generation system with purge and cryogenic pre-concentration and followed by thermal desorption and gas chromatographic separation before detection by atomic absorption spectrometer (HG-CT-GC-QAAS). A detailed description of the system can be found elsewhere (Tseng et al., 1997; Tseng et al., 1998).

### 3. Results and discussion

#### 3.1. Hydrochemical characterisation of the Valdezogues River system

Since no adequate hydrological data are available for this hydrosystem, firstly a general characterization was attempted. Pollution, both organic and heavy metals different from Hg, was evaluated.

Waters were monitored throughout the different seasons in 1995–1997 (only one in 1995). In order to fully characterise an hydrosystem it is of great interest to analyse also the substrate which the waters are in contact with. As sediments are less affected by seasonal variations they were collected only in autumn 1997.

##### 3.1.1. Waters

Twenty-four parameters were evaluated in each water sample. Due to the large amount of analytical results obtained, it is not considered suitable to include the whole. A basic statistical assessment of the results is displayed in Table 1. Oxidability is referred to organic

matter susceptible to be oxidised by permanganate, other results are expressed as ions shown in the table. Carbonate, surfactants, zinc and cadmium results are not included since values lower than our detection limits were always obtained. Mercury concentrations will be presented in the following section.

In general, waters from the Valdezogues River were slightly alkaline (mean value of  $7.74 \pm 0.74$ ) but during winter 1997 (an especially rainy period) the pH values were slightly acid, varying from 5.9 to 6.4. The drop in pH would be related to the influence of rainwater containing dissolved  $\text{CO}_2$ , and leaches humic substances. The conductivity values indicate that we are dealing with low mineralised waters. These values rise in summer and autumn drought periods since the river does not flow.

The diagrams of Piper (Piper, 1944) have allowed us to characterise the water samples according to their hydrochemical facies at the different seasons. There is a clear preponderance of sulphated (39.7%) and chlorided-sulphated (43.0%) over the bicarbonated ones (17.1%). On the other hand, all the samples were calcic-magnesian (70.3%) or magnesian (30.0%) water. Regarding the sampling station, the samples from the upper river (Points 1–4) are mainly calcic or calcic-magnesian sulphated (74.5%), while from sampling point 5 the sulfated-chlorided is clearly predominant (66.5%). This increase in chloride content could be related to waste urban water that enters in points 5 and 8.

The organic pollution is quite serious for some local situations. Values up to  $5.9 \text{ mg l}^{-1}$  of phosphate,  $1.42 \text{ mg l}^{-1}$  of nitrite and  $12.0 \text{ mg l}^{-1}$  of ammonium have

been measured in points 5 and 8 that receive waste urban waters without any treatment. During the 2 years the same trend was observed, with maximum values of the organic pollution parameters in summer and autumn, while in winter and spring an autodepuration occurs as a consequence of raining. The oxidability, in general, does not reach very high values, reflecting in some case situation where anoxia can appear (oxidability  $> 12 \text{ mg l}^{-1}$ , 2% of the samples).

With regard to metals, only manganese and iron levels are high. Their contents follow the same trends that organic pollution. The maximum levels ( $4.10 \text{ mg l}^{-1}$  for manganese and  $2.57 \text{ mg l}^{-1}$  for iron, respectively) are found close to areas of mining activity (points 1 and 9).

To quantify the quality of waters in an objective way, the statistical indexes of Harkins have been calculated (Harkins, 1974). To evaluate the combined effect of certain related parameters, the “indexes of partial quality” (IPQ) have been obtained as an average of the scores corresponding to the grouped parameters and then normalised (that is, expressed as a percentage with regards to the total sum of all individual indexes in all points). Four types of partial indexes have been defined: (1) non-specific parameters (pH and conductivity); (2) organic pollution (oxidability, nitrate, nitrite, ammonium, phosphate); (3) pollution by metals (trace metals excepted Hg); and (4) major components (remaining anions and cations).

The seasonal evolution of the IPQ is shown in Fig. 2a. The worst quality corresponds to autumn 1995 in spite of the fact that no organic pollution parameters were determined. This is because the effects of a long drought period are still evident. For the two complete years analysed the same trend is observed, that is water quality deterioration occurs in summer and autumn mainly due to major components and organic pollution.

In Fig. 2b the spatial distribution of the IPQ is represented. The non-specific parameters have a very similar behaviour. The partial index related to organic pollution presents the maximum levels in points 5 and 8, this is related to sewage inputs. The index of pollution by metals has the maximum values in points 1 and 9, it confirms the influence of mining activities previously stated.

### 3.1.2. Sediments

Following the characterization of this hydrosystem, nine sediment samples, collected at the same points that waters, were subjected to analysis. Twenty-four parameters were evaluated and the results are shown in Table 2.

Carbon contents do not exceed 2% and organic nitrogen and phosphorus are also low (Table 2). These values show the non-organic character of these sediments, this fact has important implication for the geochemistry of mercury and other pollutant in the studied system.

Table 1

Interval and mean values  $\pm$  standard deviation of the studied parameters in water samples from the Valdezogues River ( $\text{mg/l}$ )

| Parameters                         | Interval     | Mean value $\pm$ SD ( $n$ ) <sup>a</sup> |
|------------------------------------|--------------|--|
| pH                                 | 9.50–5.87    | $7.74 \pm 0.74$ ( $n = 75$ )             |
| Temperature ( $^{\circ}\text{C}$ ) | 29.0–8.70    | $16.9 \pm 5.75$ ( $n = 61$ )             |
| Conductivity <sup>b</sup>          | 2310–102.8   | $513.3 \pm 363.8$ ( $n = 75$ )           |
| Calcium                            | 216–8.0      | $40.2 \pm 33.6$ ( $n = 75$ )             |
| Magnesium                          | 266–5.35     | $34.0 \pm 36.5$ ( $n = 75$ )             |
| Sodium                             | 160–6.31     | $24.2 \pm 3.48$ ( $n = 75$ )             |
| Potassium                          | 16.9–0.8     | $3.05 \pm 3.48$ ( $n = 75$ )             |
| Sulphate                           | 1678–15.8    | $150.6 \pm 234.1$ ( $n = 75$ )           |
| Chloride                           | 221–8.20     | $30.7 \pm 32.2$ ( $n = 75$ )             |
| Bicarbonate                        | 527–32.7     | $119.8 \pm 84.8$ ( $n = 75$ )            |
| Nitrate                            | 74.9–< 1.0   | $6.36 \pm 11.9$ ( $n = 75$ )             |
| Nitrite                            | 1.42–< 0.025 | $0.10 \pm 0.30$ ( $n = 62$ )             |
| Ammonium                           | 12.0–< 0.025 | $0.43 \pm 1.96$ ( $n = 62$ )             |
| Phosphate                          | 5.9–< 0.30   | $0.34 \pm 1.08$ ( $n = 62$ )             |
| Oxidability <sup>c</sup>           | 23.6–3.40    | $8.22 \pm 4.21$ ( $n = 70$ )             |
| Iron                               | 2.57–0.02    | $0.27 \pm 0.35$ ( $n = 75$ )             |
| Manganese                          | 4.10–0.03    | $0.28 \pm 0.56$ ( $n = 75$ )             |
| Copper                             | 0.05–< 0.001 | $0.002 \pm 0.006$ ( $n = 75$ )           |
| Lead                               | 0.01–< 0.001 | $0.001 \pm 0.002$ ( $n = 75$ )           |

<sup>a</sup>  $n$  = Number of samples accounted for the mean.

<sup>b</sup>  $\mu\text{S/cm}$ .

<sup>c</sup>  $\text{mgO}_2/\text{l}$ .

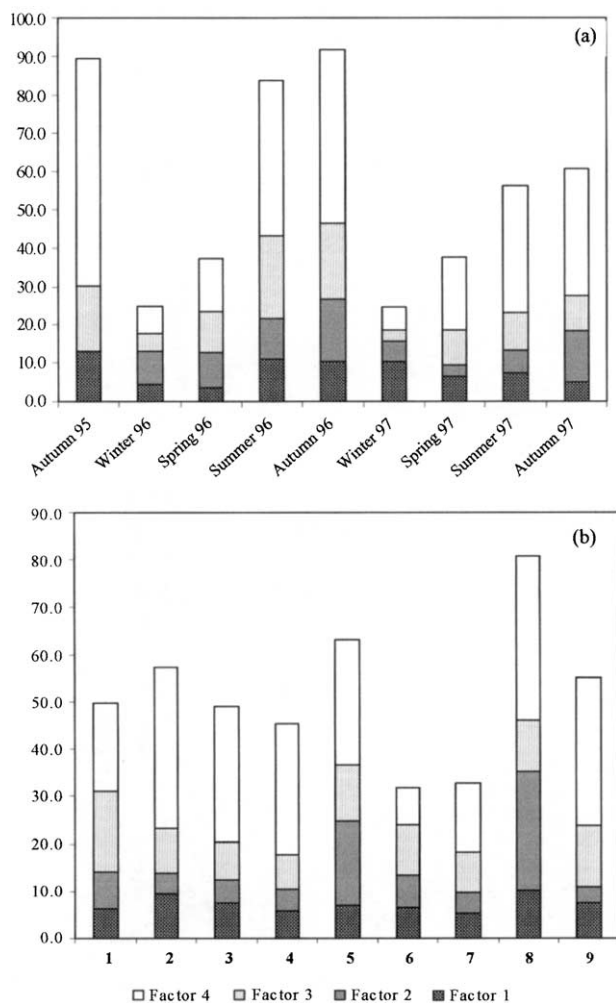


Fig. 2. Harkins' partial indexes of quality of waters (IPQ values): (a) seasonal evolution and (b) spatial variation.

The ranges of major element concentrations indicate a dominance of clay aluminium–silicate matrix (Table 2). The content of iron oxides and manganese measured in the sediments are elevated. These high values (reaching 15% of  $\text{Fe}_2\text{O}_3$ ) show that oxi-hydroxides may play an important role on the chemistry of metallic-pollutants in the Valdezogues River.

Site 9 shows high levels of all metals analysed, especially manganese and copper. Site 2 has also high contents of copper while in sites 5 and 8 the worst situation corresponds to zinc and lead.

As a methodology for assessing the pollution level of heavy metals in this aquatic environment, a comparison will be made of the geoaccumulated indexes ( $I_{\text{geo}}$ ). First introduced by Müller (1979), they are now widely adopted by workers in the field of environmental pollution (Barrocas and Wasserman, 1998; Müller and Furrer, 1995). The  $I_{\text{geo}}$  takes into account the measured concentration of the element ( $C_n$ ) and the background value ( $B_n$ ) in natural (pre-civilization, pre-industrial) pelitic sediments (Turekian and Wedepohl, 1961). Hence,

Table 2

Results corresponding to the metal contents of Valdezogues River sediments (interval and mean value  $\pm$  standard deviation)

| Parameters   | Interval  | Mean value $\pm$ SD ( $n=9$ ) |
|--|-----------|-------------------------------|
| <i>General characterization</i>                      |           |                               |
| pH   | 4.50–7.67 | 6.74 $\pm$ 0.98               |
| Conductivity ( $\mu\text{S}/\text{cm}$ )             | 77.3–896  | 347 $\pm$ 235                 |
| Loss at 500 °C (%)                                   | 1.26–6.24 | 4.37 $\pm$ 1.58               |
| Loss at 900 °C (%)                                   | 0.96–3.18 | 1.83 $\pm$ 0.73               |
| $\text{CO}_3^{2-}$ (%)                               | n.d.      | n.d.                          |
| $\text{C}_{\text{org}}$ (%)                          | 0.30–1.95 | 0.67 $\pm$ 0.42               |
| $\text{SO}_4^{2-}$ (%)                               | 0.36–1.37 | 0.53 $\pm$ 0.33               |
| $\text{NH}_4^+$ ( $\mu\text{g}/\text{g}$ )           | 9.29–49.4 | 16.7 $\pm$ 15.6               |
| $\text{NO}_2^-$ ( $\mu\text{g}/\text{g}$ )           | n.d.–0.69 | 0.17 $\pm$ 0.22               |
| $\text{NO}_3^-$ ( $\mu\text{g}/\text{g}$ )           | n.d.–35.6 | 12.4 $\pm$ 11.1               |
| NTK ( $\mu\text{g}/\text{g}$ )                       | n.d.–2308 | 988.4 $\pm$ 972.9             |
| $\text{P}_{\text{total}}$ ( $\mu\text{g}/\text{g}$ ) | 98.1–1524 | 735.1 $\pm$ 474.5             |
| <i>Metal content</i>                                 |           |                               |
| $\text{SiO}_2$ (%)                                   | 43.5–77.5 | 64.7 $\pm$ 11.2               |
| $\text{Al}_2\text{O}_3$ (%)                          | 6.31–23.6 | 13.8 $\pm$ 5.8                |
| CaO (%)  | 0.35–0.89 | 0.59 $\pm$ 0.21               |
| MgO (%)  | 0.63–1.61 | 1.07 $\pm$ 0.36               |
| $\text{Na}_2\text{O}$ (%)                            | 0.56–1.30 | 0.82 $\pm$ 0.23               |
| $\text{K}_2\text{O}$ (%)                             | 0.86–2.78 | 1.73 $\pm$ 0.57               |
| $\text{Fe}_2\text{O}_3$ (%)                          | 6.14–15.3 | 9.13 $\pm$ 2.80               |
| Zn ( $\mu\text{g}/\text{g}$ )                        | 94.4–216  | 150 $\pm$ 41.5                |
| Mn   | 187–3194  | 672.8 $\pm$ 952.1             |
| Cu   | 18.0–118  | 42.2 $\pm$ 33.6               |
| Cd   | <0.5–0.94 | 0.10 $\pm$ 0.31               |
| Pb   | 15.4–60.2 | 35.0 $\pm$ 15.4               |

n.d., not detected.

the  $I_{\text{geo}}$  in class 0 indicates absence of contamination, and the  $I_{\text{geo}}$  in class 6 represents the upper limit of maximum contamination. The background concentrations (in  $\mu\text{g}/\text{g}$ ) of the heavy metals considered in this study are: zinc, 95; manganese, 850; copper, 13.5; cadmium, 0.30; lead, 20.0.

The vast majority of samples correspond to  $I_{\text{geo}}$  in class 0, which indicates no contamination. However, there are some exceptions, stations 5 and 8 fall into  $I_{\text{geo}}$  class 1 for lead and zinc. This could be related to the sewage discharges detected in waters. The stations 2 and 9 are also classified in the level  $I_{\text{geo}}=1$  for lead, zinc and copper. The strongest contamination corresponds to station 9 for manganese with a  $I_{\text{geo}}=2$ .

### 3.2. Evaluation of the present mercury pollution state

Mercury pollution has been evaluated with respect to general standards proposed for uncontaminated areas and by comparison with Hg data found in recent literature for other areas exposed to pollution. Background levels for sediments from the Valdezogues River have been also determined.

The Carson River System (Nevada, USA); Kuskokwin River Region (South-western Alaska); Idrija (Slovenia) and Monte Amiata (Italy) localisations have been

selected for comparison because they have some similarities with the Valdezogues River, including: their location in a mercuriferous belt (North America and Mediterranean areas) and their Hg pollution related to mining activities. Additionally, these sediments are not organic-rich (e.g. Total Organic Matter for Carson River 1–2%) and the pH of waters are alkaline. In the Carson River System the contamination is a legacy of processing the gold and silver ores using amalgamation with mercury as extraction procedure between 1860 and 1890. To the Carson River arrive the alluvial fan from the adjacent Six Mile Canyon, where mining activities took place. In the south-western Alaska and Monte Amiata areas the antropogenic source of mercury is mercury mine exploitation, although neither the duration nor the production are comparable with the Almadén mine. The most similar case to Almadén is the Idrija Mine, this is the second largest Hg mine in the world which operated for 500 years with a production of over 5 million t of Hg. However, the main distinction between all of these areas and Almadén is that they are not active anymore.

Mercury data obtained in the present study have been also compared with those corresponding to the survey performed in the Almadén area between 1974 and 1977. Although the main source of mercury to the aquatic environment has changed and the sampling strategy is not coincidental, there are still four common sampling stations for comparison.

### 3.2.1. Mercury in waters

Mercury concentration was determined in water samples collected seasonally through 1995 and 1997. The results are shown in Table 3. In general, levels in water are lower than our detection limits (0.11 µg/l, calculated as three times the standard deviation of 10 blanks). However, some water samples from station 9 had extremely high mercury concentrations (up to 20.3 µg/l in summer 1996). This station indicates the impact of very recent mine tailings, corresponding to Las Cuevas mine, and the spatial and temporary variations were checked. In the sampling corresponding to spring 1996 a first sample was collected at station 9 and the mercury concentration was determined to be 2.0 µg/l. This sampling was repeated a week after, also spring, and the mercury concentration was 18.7 µg/l. Additionally two samples were taken, 50 m above and below the station 9. The mercury concentration in the sample collected above was not detectable while the sample collected below was 8.24 µg/l. It seems that water responds quickly to direct mercury inputs, but after mercury levels also rapidly decrease with respect to both spatial (not detectable–18.7–8.24 µg/l in 100 m) and temporary (from 2.0 to 18.7 µg/l within a week) variations.

Almost all concentrations of mercury in stream water samples collected in the Valdezogues River are below

Table 3

Total mercury concentrations in waters (interval) and sediments (mean ± standard deviation) from Almadén area

| Sampling station | Water (µg/L)             | Sediment (µg/g)          |
|------------------|--------------------------|--------------------------|
| 1                | <D.L. <sup>a</sup> –0.62 | 15.9 ± 1.59 <sup>b</sup> |
| 2                | <D.L.–1.13               | 60.0 ± 3.93              |
| 3                | <D.L.–0.69               | 68.6 ± 1.38              |
| 4                | <D.L.                    | 65.6 ± 3.66              |
| 5                | <D.L.                    | 78.9 ± 1.65              |
| 6                | <D.L.                    | 5.53 ± 0.69              |
| 7                | <D.L.                    | 74.4 ± 1.70              |
| 8                | <D.L.–0.68               | 107.2 ± 2.72             |
| 9                | <D.L.–20.3               | 1005 ± 96.1              |
| A                | –                        | 0.57 ± 0.14              |
| B                | –                        | 0.52 ± 0.13              |
| C                | –                        | 14.84 ± 0.82             |

<sup>a</sup> D.L., Detection limit.

<sup>b</sup> Mean of three independent determinations.

both the 2.4 µg/l maximum in-stream concentration recommended by the US Environmental Protection Agency (EPA, 1992) and the European Union's suggested maximum allowable concentration of 1.0 µg/l total Hg (average monthly) for inland surface waters.

These results are consistent with the values found in the other areas selected for comparison. Total mercury concentrations in unfiltered surface water from the Carson River ranged from 0.053 to 0.592 µg/l (sampling carried out in August and September 1993; Gustin et al., 1994). Stream-water samples collected downstream from two mines (Red Devil and Cinnabar Creek) in the south-western Alaska study contained as much as 0.28 µg/l Hg in raw unfiltered stream-water samples. In all filtered water samples collected downstream from the mines, Hg concentrations are less than 0.10 µg/l and similar to mercury concentrations in stream-water samples collected from background sites (Bailey and Gray, 1995). For the Monte Amiata area a maximum concentration value of 0.010 µg/L was measured, this value refers to the total mercury (dissolved + particulate). These concentrations are comparable to those obtained by the same authors for other watercourses of the Italian peninsula that drain unmineralized areas (Ferrara et al., 1991). At the Idrija area, total mercury concentrations in unfiltered water samples increase from <0.003 µg/l just upstream of the mining district to over 0.300 µg/l within the town of Idrija. Hg concentration decreases downstream the mine and Gulf of Trieste water near the river mouth (100 km downstream) contained up to 0.065 µg/l total Hg (Horvat et al., 1999).

Several factors have been accounted for the low mercury concentrations generally found in waters even downstream from sources, such as the high volatile nature of mercury or its tendency to be sorbed by clays, iron and manganese hydroxides and organic matter (Jenne, 1970). The alkaline pH (Carson River pH 7.3–8.7) is also an important factor since most studies have

shown an inverse relationship between pH and mercury bioavailability (Miskimmin, 1992).

The mercury concentrations found in the station 9, situated in a stream adjacent to Las Cuevas mine (the only in intermittent activity nowadays), are among some of the highest reported values. For example, maximum mercury concentrations of 35.4 µg/l were reported for Six Mile Canyon (adjacent to areas with highly contaminated tailings) in the Carson River System (Gustin et al., 1994).

With respect to mercury levels for the Almadén area in 1974–1977, extremely elevated total mercury concentrations ( $354.0 \pm 147.3$  µg/l) were found in the station placed just where the mine liquid effluent from the Almadén mine were discharged. These values give a measure of the amount of mercury discharged in the rivers during the period of mining activity and before the installation of the effluent treatment plant. Total mercury concentration in water decreased downstream to the confluence with the Valdezogues River. The concentration in unfiltered water samples from this river ranged between 1.64 and 3.00 µg/l.

### 3.2.2. Mercury in sediments

Superficial sediments collected from the Valdezogues River, at the same sampling stations as water, exhibited nearly a three-order of magnitude range in mercury concentration from 5.53 to 1005 µg/g (Table 3). Not surprisingly, total-mercury concentrations are significantly higher in the station 9 (up to 1005 µg/g). The mercury concentration in the other sediments ranged from 5.53 to 107 µg/g. Total mercury levels show an increasing trend along Valdezogues River: from 60.0 µg/g in the station 2 to 107.2 µg/g in the station 8. However, there are two stations whose concentrations were considerably lower than these values (15.9 and 5.53 µg/g for sites 1 and 6, respectively). These last stations correspond to two dams built in Valdezogues River. It could be related to the fact that at these stations sediments correspond to recent flooded soils and not to real river sediments.

In respect with the relation between mercury levels in sediments and the other parameters studied, it can be observed a very high correlation ( $r=0.82$ ) for Zn and Hg (taking out station 9). This is coherent with the fact that both of these metals are associated in sulphur mineralizations.

In Table 3 are also included the mercury contents for the three additional stations selected in the sediments study (see Fig. 1). The low mercury content in stations A and B is consistent with the lack of known mercury sources. Therefore, these sediments seem to represent an adequate background control for this area. The sample taken downstream from the Valdezogues River (Site C) confirms the distribution of mercury after the mining activities.

Taking into account that we are within a mercuriferous belt, an attempt to evaluate regional background levels for mercury was done. Mercury concentrations in sediment samples from sites not directly affected by mining activities were 0.53 and 0.57 µg/g in stations A and B (Fig. 1), respectively. These values for regional background mercury concentrations are one order of magnitude higher than those normally cited as representative of global background (0.01–0.05 µg/g) (Andersson, 1979; Gustin et al., 1994). The elevated “geological background” concentration is a consequence of the natural mercury enrichment in the area, although possible airborne contamination of the control stations is also accounted for this observation. All the sediment concentrations measured during this study are considerably elevated above the background values, which indicates an impact of mining activities.

The coexistence of contaminated and non-contaminated areas in the studied system gives an opportunity for comparison with data obtained elsewhere. Background values and mercury distribution in sediments from the selected literature are given in Table 4. High regional background values of mercury are reported for all of these exposed areas and they are similar to those found at the Almadén area. Again, mercury concentrations in sediments from the Valdezogues River are among the highest reported values. For instance, the Carson and the Valdezogues River show the same range of concentrations (2–150 and 5–107 µg/g, respec-

Table 4  
Total mercury and background concentrations in some polluted mining areas

| Location  | Mercury concentration (µg/g) | Reference               |
|---|------------------------------|-------------------------|
| <i>Carson River Drainage Basin of Nevada, EEUU</i>  |                              |                         |
| Background sediment/soil                            | 0.1–0.6                      | (Gustin et al., 1994)   |
| Carson River  | 2–156                        |                         |
| Six Mile Canyon                                     | 2.9–1610                     |                         |
| <i>Kuskokwin River Region, South-western Alaska</i> |                              |                         |
| Cinnabar Creek mine                                 |                              |                         |
| Background soil                                     | 0.16–1.2                     | (Bailey and Gray, 1995) |
| Soil mine area                                      | 110–1500                     | (Bailey and Gray, 1995) |
| Stream-sediment                                     | > 36                         | (Gray et al., 1996)     |
| Red Devil mine                                      |                              |                         |
| Background soil                                     | 0.10–0.39                    | (Bailey and Gray, 1995) |
| Soil mined area                                     | 0.15–1200                    | (Bailey and Gray, 1995) |
| Overall stream-sediment background                  | <0.45                        | (Gray et al., 1996)     |
| <i>Monte Amiata, Italy</i>                          |                              |                         |
| Soil  |                              | (Ferrara et al., 1991)  |
| Tuscany (background)                                | 0.05–0.50                    |                         |
| Monte Amiata  | 0.07–1379                    |                         |
| Sediment  |                              |                         |
| Tuscany (background)                                | 0.05–1.0                     |                         |
| Monte Amiata  | 3–10                         |                         |



tively) and mercury levels in areas directly affected by mine tailings are of the same order: up to 1610 µg/g in Six Mile Canyon (Carson River System) and 1005 µg/g (Station 9, close to Las Cuevas mine) in the present study. Mercury levels in sediments from the Idrija River ranged between 2 µg/g upstream of the town of Idrija and up to 1000 µg/g within the area. Further downstream, the sediments contain lower mercury concentrations (from 5 to 300 µg/g; Gosar et al., 1996). These results confirm the high concentration of Hg (815 µg/g) previously reported by Hess (1991) in the sediments of the Idrija River. All these total mercury concentrations are significantly higher than those reported for the Monte Amiata region. Ferrara et al. (1991) have stated that for this area few years after the closing of the mines the mercury levels have returned to the natural background of this region, with the exception of the zones where roasted cinnabar was deposited.

A summary of the mercury concentrations in the common stations sampled in the present study and in the 1974–1977 period at the Almadén area is shown in Table 5. It is observed a general diminution. The last 20 years of decreasing activity and the installation of a mine wasting treatment plant in 1977 may account for this fact.

The values corresponding to the station C, established downstream from the Valdezogues River and just before the confluence to La Serena dam, confirms the distribution of mercury after the mining activities in both periods (Table 5). This dam has been recently built to supply water for agricultural irrigation, and thereafter, it received the bulk of sediment transported downstream by the Valdezogues River. Bio-magnification mercury processes are likely to occur in this big water reservoir (3231 Hm<sup>3</sup>) and it should be further investigated.

Chemical availability of mercury in these sediments has been previously reported (Rodríguez et al., 2000). The chemical speciation, fractionation and availability of mercury in sediments were studied with different extraction and analytical procedures. One specific sequential extraction procedure was applied in order to evaluate the geochemical partitioning of mercury in

sediments. The sequential extraction results indicate that forms associated to the “sulfidic phase” and “residual phase” play a significant role in the chemical immobilization of mercury in these sediments. No organo-mercury compounds (i.e. mono and di-methylmercury) were detected (< 2 µg/g). Although it has been demonstrated that mercury in Almadén’s sediments is not available, and no methylation at a detectable level was found, the elevated concentrations of mercury in the sediments of the Valdezogues River confirm that this stream is a major source of mercury for the aquatic environment in the region.

### 3.2.3. Mercury in bivalves

Total mercury concentrations have been measured both using an acid treatment in closed microwave system and CV-AAS detection and TMAH digestion in an open-microwave system and HG-CT-GC-QAAS detection, following the preparation and analytical procedure described in the experimental section. This last system has been also used for the determination of monomethylmercury. Mercury concentrations (both inorganic and monomethylmercury) in bivalves are provided in Table 6, along with location, season and number of individual information.

Total mercury values found by CV-AAS analysis ranged between 1.57 and 4.10 µg/g. A good agreement was found with those values (1.57–5.76 µg/g) obtained by TMAH treatment. Between 20 and 40% of the total mercury is present as monomethylmercury.

The restricted number of organisms and the fact that few were common for more than a season make it meaningless to try to compare mercury concentration at different sites within the Valdezogues River. We can, nevertheless, contrast the mercury levels found by us (Table 6) with those reported as safety limits for human consumption and those values reported for other polluted areas.

Taking into account that the average dry weight of an analysed sample was 25% of the fresh one, the vast

Table 5  
Comparison of total mercury contents (µg/g) for Valdezogues River sediments in 1974–1977 and 1995–1997 periods

| Sampling station | ORNL study <sup>a</sup> | Present study <sup>b</sup> |
|------------------|-------------------------|----------------------------|
| 5                | 157±51                  | 78.9±1.65                  |
| 8                | 1085±681                | 107.2±2.72                 |
| B                | 515±136                 | 0.52±0.13                  |
| C                | 203±88                  | 14.8±0.8                   |

<sup>a</sup> Mean of the <105-µm sediment size fraction from spring 1976, autumn 1976 and spring 1977.

<sup>b</sup> Mean of three independent determinations of the <2-mm fraction from autumn 1997.

Table 6  
Total mercury and monomethylmercury concentration in freshwater bivalves determined by CVAAS and HG-CT-GC-QAAS

| Sample | Acid treatment<br>CVAAS<br>detection | TMAH treatment<br>HG-CT-GC-QAAS |                         | Sampling station,<br>season, number<br>of individuals |
|--------|--------------------------------------|---------------------------------|-------------------------|---|
|        |                                      | Hg <sub>total</sub> (µg/g)      | Hg <sup>2+</sup> (µg/g) |   |
|        |                                      |                                 | MMHg<br>(µg/g) %        |   |
| 1      | 4.10                                 | 3.09                            | 2.67                    | 46.3 1; spring 96; n=4                                |
| 2      | 3.22                                 | 3.07                            | 0.67                    | 17.9 4; autumn 96; n=3                                |
| 3      | 4.13                                 | —                               | —                       | — 4; summer 96; n=6                                   |
| 4      | 4.60                                 | 3.05                            | 1.19                    | 28.1 4; summer 97; n=5                                |
| 5      | 2.80                                 | 2.29                            | 1.43                    | 38.4 6; spring 96; n=6                                |
| 6      | 1.31                                 | 0.98                            | 0.59                    | 37.6 7; summer 96; n=4                                |

majority of the Valdezogues River bivalves have an average Hg content over or close to the maximum limit permissible level according to WHO (0.5 µg/g) for edible parts of marine organisms (WHO-IPCS, 1990).

All the reported values are considerably high if they are compared with the typical concentration of mercury in aquatic invertebrates from uncontaminated areas, which is generally less than 0.1 µg/g wet weight (Cox et al., 1975; Phillips et al., 1987; Allard et al., 1989). Tissue concentrations over 1 µg/g ww are reported for areas with antropogenic point sources of mercury. Thus, values in the range 0.11–2.52 µg/g (dry weight) for bivalves were reported in a study of mercury concentrations carried out in benthic organisms from an estuary contaminated by chlor-alkali plant (Palmer et al., 1996).

Very interesting for our own case is the long-term study involving annual testing of the natural and mining-induced contamination of the Plagia River (at the Monte Amiata area) carried out by Bacci et al. (1978) using the fresh-water mussel *Unio elongatus*. The total concentration in abductor muscles of mussels collected in one sampling station was evaluated from 1973 to 1976. In 1973 the mercury concentration was very high (1.6 µg/g ww), an order of magnitude higher than the concentrations found for the same organism in other Italian rivers. From 1973 to 1975 there is sharp decrease in the Hg levels in the mussel in connection with the closing of many mines and the installation of purification equipment in 1973. After 1975 the mercury concentration remains constant (0.3 µg/g ww) 2–3 times higher than the background ones.

With respect to mercury speciation, the percentage of mercury that is methylated varies from 17 to 40%. This represents a high accumulation factor with respect to sediments. Previously it was demonstrated that mercury in Almadén's sediments were not available and no methylation at a detectable level was found (Rodríguez et al., 2000). However, these results are consistent with earlier studies involving marine bivalves on phytoplankton as well as other invertebrates and fish. In mussels inhabiting different sites with varying degrees of mercury contamination, the percentage of total mercury that is methylated can vary from 17 to near 100%, with the highest percentages of methylmercury in relatively unpolluted areas (Mikae et al., 1985; Riisgard et al., 1985). The inorganic/methylmercury ratios in mussels can in part be explained by the greater depuration rates of inorganic mercury than methylmercury (Gagnon and Fisher, 1997).

Although the data are limited and it is difficult to estimate a sediment/organisms concentration factor, the result of this first ever benthic infauna study in Valdezogues River showed that the contaminated sediments are almost certainly a continuing source of mercury to organisms. It has resulted in elevated concentrations in the biota, tissue concentrations are values of the same

order than those reported of other areas with antropogenic point sources of mercury.

## Acknowledgements

R. C. Rodríguez is grateful to the Spanish Government for her PhD Fellowship (B.O.E. 01.12.1995). The authors thank O.F.X. Donard (Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, CNRS UMR 5034, Pau, France) for allowing us to use its facilities for mercury speciation analysis.

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